



Publication number: **0 515 195 A1**

EUROPEAN PATENT APPLICATION

Application number: **92304636.1**

Int. Cl.⁵: **C08L 83/06, D06M 15/643, A61K 7/06, A61K 7/48**

Date of filing: **21.05.92**

Priority: **24.05.91 US 705454**

Date of publication of application: **25.11.92 Bulletin 92/48**

Designated Contracting States: **BE DE FR GB IT NL SE**

Applicant: **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, NY 12345 (US)

Inventor: **Thimlineur, Raymond Joseph**
162 Willow Lane
Scotia, New York 12302 (US)
Inventor: **Traver, Frank John**
1 Downey Road
Troy, New York 12180 (US)
Inventor: **Vanvalkenburgh, Virginia Mary**
Box 133, Schoolhouse Road
West Lebanon, New York 12195 (US)

Representative: **Pratt, Richard Wilson et al**
London Patent Operation G.E. Technical
Services Co. Inc. Essex House 12/13 Essex
Street
London WC2R 3AA (GB)

Liquid silicone esters.

The present invention provides a silicone ester having a melting point of up to about 30°C., and comprising (A) units of the general formula $R_aR^E_bSiO_{[4-(a+b)]/2}$ or (B) $R_xR^E_ySiO_{1/2}$ units and $SiO_{4/2}$ units; R^E being an ester-containing organic group. The silicone ester is liquid at ambient skin temperature and has improved workability, improved payout, improved emollient properties, greater solubility in organic compounds, greater substantivity to surfaces and improved water resistance.

EP 0 515 195 A1

Background of the Invention

The present invention relates to silicone esters. More particularly, the present invention relates to liquid silicone esters which are useful in personal care products.

The usefulness of silicone ester waxes in personal care products is disclosed in U.S. Patent No. 4,725,658 to Thayer et al (Thayer). These waxes have melt points which are higher than skin temperature, skin temperature being about 25°C-30°C. Because the silicone esters disclosed in the Thayer patent are not liquid at skin temperature, they are generally hard, brittle materials which are difficult to work with and difficult to spread and apply.

It would be desirable therefore to provide a silicone ester having a melting point which is lower than skin temperature, i.e., less than 30°C, and, consequently, has improved workability and better payout, i.e., spreads out more readily on skin, hair, or other surfaces.

In addition, it would be desirable to provide a silicone ester having improved emollient properties and greater solubility in organic compounds.

It would further be desirable to provide a silicone ester having greater substantivity to surfaces and improved water resistance.

Summary of the Invention

The present invention provides a silicone ester composition comprising a silicone ester or blend of silicone esters, the silicone ester or blend of silicone esters having a melting point of up to about 30°C., and comprising:

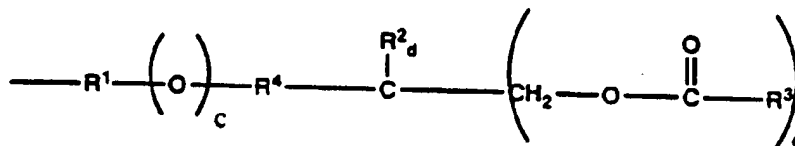
(A) units of the general formula:



wherein R is an organic radical, a is a number ranging from 0 to 3, b is a number ranging from 0 to 3, a+b is a number ranging from 1 to 3, with the proviso that there is present at least one R^E radical, R^E being an ester-containing organic group selected from the group consisting of:

(1)

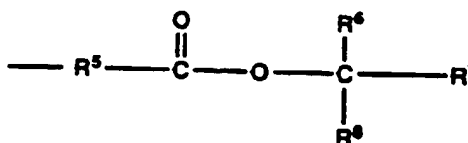
(II)



wherein c is 0 or 1; d is 0, 1, or 2; e is 1, 2, or 3; the sum of d+e being 3; further wherein R¹ is a linear or branched organic group having from 2 to about 14 carbon atoms if the ester-containing organic group (1) contains no olefinic unsaturation and R¹ is a linear or branched organic group having from about 2 to about 18 carbon atoms if the ester-containing organic group (1) contains olefinic unsaturation; further wherein R² is hydrogen or an organic radical of from 1 to about 6 carbon atoms; R³ is a linear unsaturated organic radical of from 1 to about 23 carbon atoms, a linear saturated organic radical of from 1 to about 17 carbon atoms, or a branched organic radical of from about 1 to about 35 carbon atoms; and R⁴ is a linear or branched organic radical having 0 to about 6 carbon atoms;

(2)

(III)



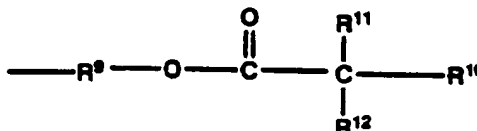
wherein R⁵ is a linear or branched organic group having from 2 to about 15 carbon atoms if the ester-con-

taining organic group (2) contains no olefinic unsaturation and R^5 is a linear or branched organic group having from 2 to about 23 carbon atoms if the ester-containing organic group (2) contains olefinic unsaturation; further wherein R^6 is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms, and R^7 is a linear unsaturated organic radical of from 1 to about 23 carbon atoms, a linear saturated organic radical of from 1 to about 17 carbon atoms, or a branched organic radical of from 1 to about 35 carbon atoms; and R^8 is hydrogen or a linear or branched organic group having from 1 to about 6 carbon atoms;

or

(3)

(IV)



wherein R^9 is a linear or branched organic group having from 2 to about 14 carbon atoms if the ester-containing organic group (3) contains no olefinic unsaturation and R^9 is a linear or branched organic group having from 2 to about 24 carbon atoms if the ester-containing organic group (3) contains olefinic unsaturation; R^{10} is a linear unsaturated organic radical of from 1 to about 22 carbon atoms, a linear saturated organic radical of from 1 to about 14 carbon atoms, or a branched organic radical of from 1 to about 34 carbon atoms; R^{11} is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms; and R^{12} is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms; or (4) chemical reaction mixtures of (1), (2), and (3);

or

(B) $R^{13}_x R^E_y SiO_{1/2}$ units and $SiO_{4/2}$ units;

wherein each R^{13} is independently an organic radical, x is a number ranging from 0 to 3, y is a number ranging from 0 to 3, $x+y$ is 3, with the proviso that there is present at least one R^E radical, R^E being an ester-containing organic group as defined in (A); the ratio of $R^{13}_x R^E_y SiO_{1/2}$ units to $SiO_{4/2}$ units being from about 0.5:1 to about 4:1.

The present invention is further directed to physical mixtures and chemical mixtures of the foregoing silicone ester liquids and to personal care or textile softening compositions containing the liquid silicone esters or mixtures thereof. The invention is further directed to methods for improving the substantivity, payout, and workability of personal care compositions by incorporating therein the silicone esters or mixtures of the silicone esters of this invention.

The liquid silicone esters of the present invention have greater substantivity to surfaces, improved water resistance, improved workability, greater payout on surfaces, improved emollient properties and greater solubility in organic compounds.

Detailed Description of the Invention

The present invention is directed to silicone esters which are liquid at skin temperature or below. The silicone esters of this invention have a melting point of up to about 30°C and preferably up to about 25°C.

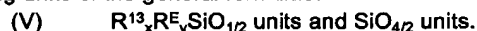
The liquid silicone esters of this invention are selected from

(A) silicone esters having units of the general formula



or

(B) silicone esters having units of the general formulae:



In formulas (I) and (V), R and R^{13} are each independently an organic radical; R^E is an ester-containing organic radical as described hereinabove; a is a number of from 0 to 3; b is a number of from 0 to 3; the sum of $a+b$ is a number of from 1 to 3; x is a number of from 0 to 3; y is a number of from 0 to 3; and the sum of $x+y$ is 3.

In formula (II), the ratio of $R^{13}_x R^E_y SiO_{1/2}$ units to $SiO_{4/2}$ units is from about 0.5:1 to about 4:1 and preferably from about 1:1 to about 3:1.

In formulas (I) and (V), radicals represented by R and R^{13} include any substituted or unsubstituted organic

radical, for example, alkyl radicals, such as methyl, ethyl, propyl, butyl, octyl, decyl, cyclohexyl, cyclopentyl, and the like; aryl radicals such as phenyl, tolyl, xylyl, naphthyl, and the like; aralkyl radicals such as phenylethyl, benzyl, and the like; or any of the foregoing wherein one or more hydrogen atoms is replaced with, for example, a halogen, cyano, amino, or the like. Most preferably, all of the R^1 and R^{13} radicals are methyl or a mixture of methyl and phenyl.

As mentioned above, the silicone esters of this invention must contain at least one R^E radical. R^E is an ester-containing organic radical selected from the group consisting of the radicals represented by Formulas (II)-(IV) above.

In the ester-containing radical of Formula (II), c preferably represents 1, d preferably represents 1, and e preferably represents 2.

The number of carbon atoms in each of the R^1 - R^{12} radicals and the branched or linear nature of the ester-containing radicals are critical to the melting point of the silicone ester, and, accordingly, to whether the silicone ester is a liquid at skin temperature.

The R^1 - R^{12} radicals represent both saturated and unsaturated organic radicals. Preferably, the R^1 - R^{12} radicals represent linear or branched alkyl or alkenyl radicals containing the number of carbon atoms recited above.

The number of carbon atoms required in the radicals represented by the R^1 , R^3 , R^5 , R^7 , R^9 , and R^{11} radicals in order to provide a silicone ester which is liquid at skin temperature in turn depends on the level of olefinic unsaturation in the ester-containing radical.

Thus, R^1 , R^5 , and R^9 are linear or branched organic groups, preferably alkyl groups, having from about 2 to about 14, preferably from about 2 to about 12, and most preferably from about 3 to about 10, carbon atoms if the ester-containing organic groups (1), (2), and (3), respectively, contain no olefinic unsaturation and R^1 , R^5 , and R^9 are linear or branched organic groups having from about 2 to about 18, preferably from about 2 to about 16, and most preferably, from about 3 to about 10 carbon atoms if the ester-containing organic groups (1), (2), and (3), respectively, contains olefinic unsaturation.

Typically, the ester-containing organic radicals of formulas (1)-(3) will have up to about 2 mole percent of olefinic unsaturation.

R^2 is hydrogen or a linear or branched organic group, preferably an alkyl group, having from 1 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3, carbon atoms.

R^3 is a linear or branched organic group, preferably an alkyl group, having from 1 to about 35, preferably from about 8 to about 25, and most preferably from about 11 to about 17, carbon atoms.

R^4 is a linear or branched organic group, preferably an alkyl group, having from 0 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3 carbon atoms.

R^6 is hydrogen or a linear or branched organic group. The preferred organic groups represented by R^6 are alkyl groups having from 1 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3 carbon atoms. Preferably, R^6 is hydrogen.

R^7 is a linear or branched organic group, preferably an alkyl group, having from 1 to about 35, preferably from about 8 to about 25, and most preferably from about 11 to about 17, carbon atoms.

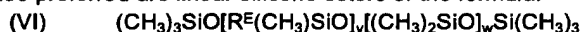
R^8 is hydrogen or a linear or branched organic group. R^8 is preferably an alkyl group having from 1 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3, carbon atoms.

R^{10} is a linear or branched organic group, preferably an alkyl group, having from 1 to about 34, preferably from about 8 to about 25, and most preferably from about 10 to about 16, carbon atoms.

R^{11} is hydrogen or a linear or branched organic group. The preferred organic groups represented by R^{11} are alkyl groups having from 1 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3, carbon atoms. Most preferably, R^{11} is hydrogen.

R^{12} is hydrogen or a linear or branched organic group, preferably an alkyl group, having from 1 to about 6, preferably from about 1 to about 5, and most preferably from about 1 to about 3, carbon atoms.

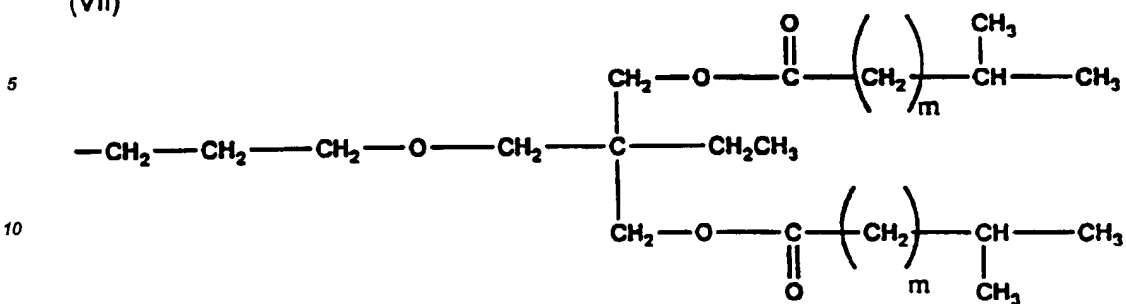
Examples of preferred silicone esters within the scope of the present invention include silicone ester resins of the general formula M'_2Q , wherein Q represents $SiO_{4/2}$ units and M' represents $R^E(CH_3)_2SiO_{3/2}$ units, wherein R^E is as defined above. Also preferred are linear silicone esters of the formula:



wherein v represents a number from 1.0 to 25, w represents a number from 0 to 100, and R^E is as defined previously herein.

Examples of preferred radicals represented by R^E include:

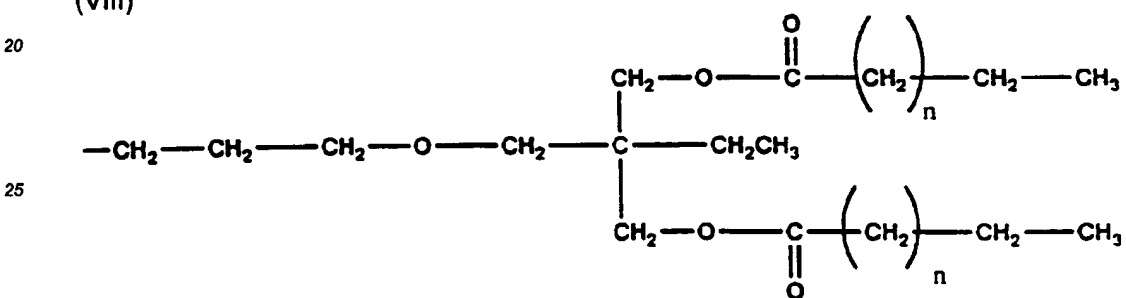
(VII)



15

wherein m is a number ranging from about 8 to about 14;

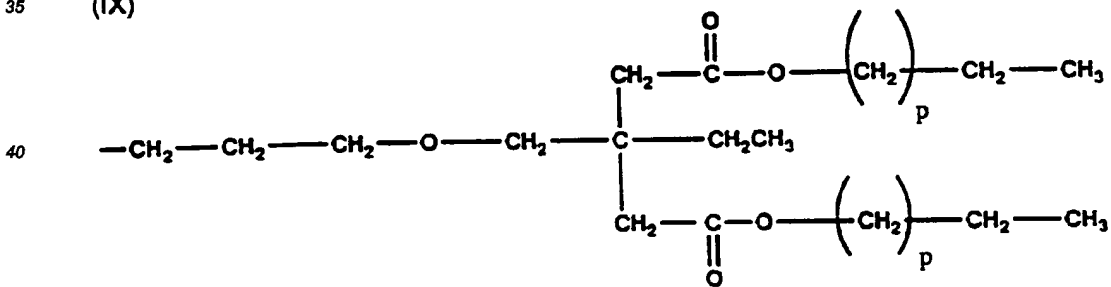
(VIII)



30

wherein n is a number ranging from about 9 to about 13;

(IX)



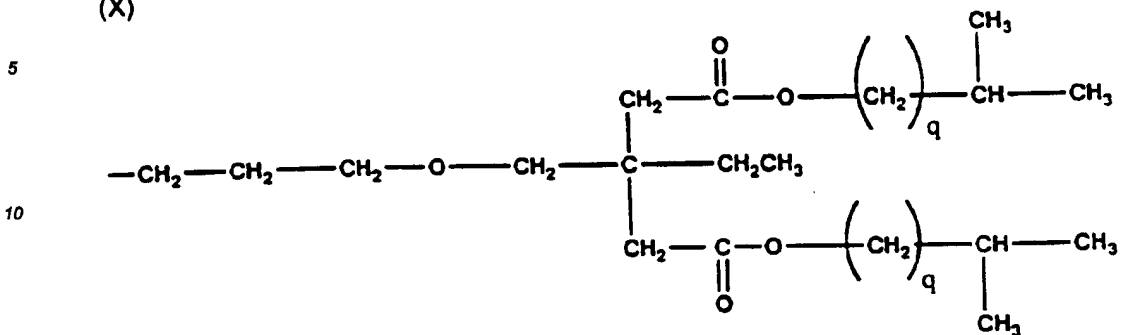
45

wherein p is a number ranging from about 10 to about 14;

50

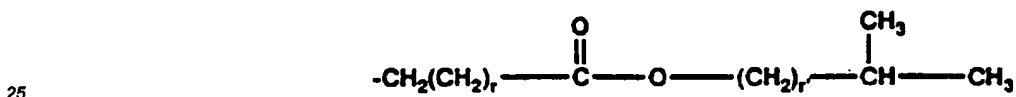
55

(X)



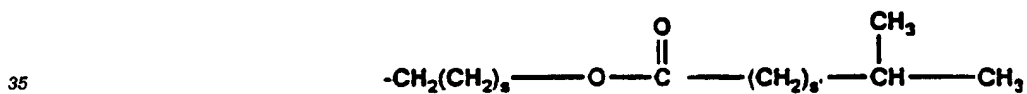
wherein q is a number ranging from about 9 to about 15;

(XI)



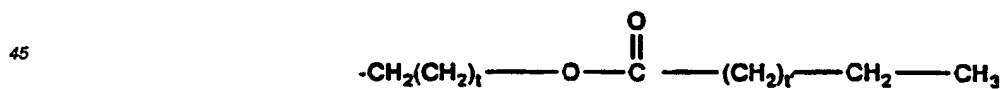
wherein r is a number ranging from about 3 to about 9 and r' is a number ranging from about 9 to about 15;

(XII)



wherein s is a number in the range of from about 2 to about 10 and s' is a number in the range of from about 8 to about 14;

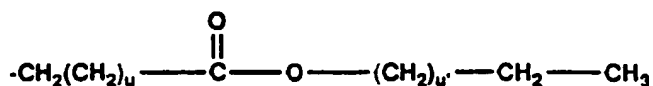
(XIII)



wherein t is a number in the range of from about 2 to about 10 and t' is a number in the range of from about 9 to about 13;

or

(XIV)



wherein u is a number in the range of from about 3 to about 9 and u' is a number in the range of from about 9 to about 14.

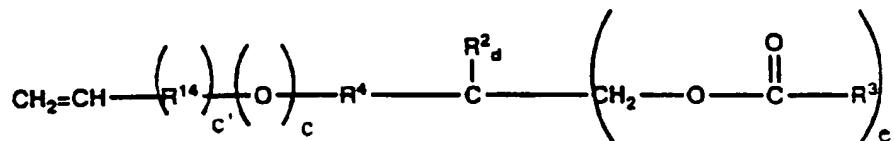
The present invention is further directed to compositions containing physical mixtures, i.e., blends, of the foregoing novel silicone ester liquids. The physical mixtures are prepared by mixing the various components at or above the melting point of all the ingredients to be used in the blend.

As mentioned hereinabove, the silicone ester of this invention has a melting point of up to about 30°C and preferably up to about 25°C. It has been found that the melting point can be as low as -60°C and even as low as -100°C when branched silicone esters are used.

The liquid silicone esters of this invention can be prepared from organohydrogenpolysiloxanes and alcohol esters of fatty acids having terminal olefinic unsaturation.

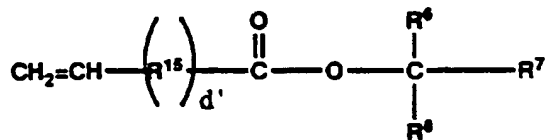
Thus, prior to reaction with an organohydrogenpolysiloxane, R^E in formulas (I) and (V) above can be represented, for example, by the general formulas:

(XV)



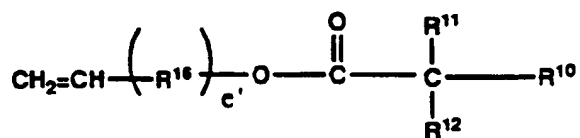
wherein R¹⁴ is an organic radical, preferably an alkylene or branched alkylene radical, having from 1 to about 12 carbon atoms if the compound of formula (XV) contains no olefinic unsaturation and from 1 to about 16 carbon atoms if the compound of formula (XV) contains olefinic unsaturation; c' is 0 or 1; and R², R³, d, R⁴, and e are as previously defined;

(XVI)



wherein R¹⁵ is an organic radical, preferably an alkylene or branched alkylene radical, having from 0 to about 12 carbon atoms if the compound of formula (XVI) contains no olefinic unsaturation and from 0 to about 16 carbon atoms if the compound of formula (XVI) contains olefinic unsaturation; d' is 0 or 1; and R⁵, R⁶, and R⁷ are as previously defined:

(XVII)



wherein R^{16} is an organic radical, preferably an alkylene or branched alkylene radical, having from 0 to about 12 carbon atoms if the compound of formula (XVII) contains no olefinic unsaturation and from 0 to about 16 carbon atoms if the compound of formula (XVII) contains olefinic unsaturation: v is 0 or 1; and R^{10} , R^{11} , and R^{12} are as previously defined;

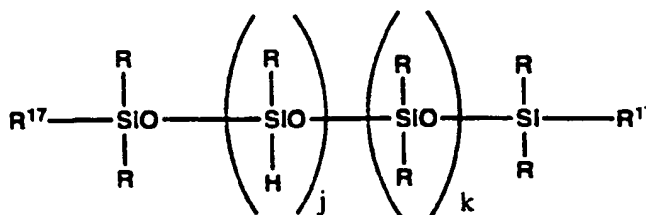
The olefinic esters of formulas (XV)-(XVII) can be prepared by reacting an alcohol with a carboxylic acid having terminal olefinic unsaturation, or, alternatively, by reacting an alcohol having terminal olefinic unsaturation with a carboxylic acid. The alcohol and the acid may be branched or linear, or one may be branched and the other linear.

Examples of alcohols suitable for making the liquid silicone esters of this invention include trimethylolpropane monoallylether (TMPMAE), stearyl alcohol, and octyl alcohol. Trimethylolpropane monoallylether is preferred. Examples of suitable acids for making the liquid silicone esters of this invention include palmitic acid, myristic acid, lauric acid, isostearic acid, and undecylenic acid. Lauric acid and isostearic acid are preferred.

It should be understood that R^E , prior to reaction with organohydrogenpolysiloxane, must contain the number of carbon atoms recited above so as to impart a liquid consistency to the composition of formulas (I) and (II) and must also contain terminal olefinic unsaturation. The terminal olefinic unsaturation allows the organic ester (i.e. R^E) to be added to the organohydrogenpolysiloxane in the presence of a hydrosilation catalyst.

The organohydrogenpolysiloxanes useful for making the silicone esters of this invention may be linear or resinous. The linear organohydrogenpolysiloxane polymers preferably have the formula

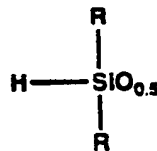
(XVIII)



wherein R is as previously defined herein, R^{17} is hydrogen or R , and j and k vary such that the polymer has a viscosity of from about 5 to about 1000 centipoise at 25°C., with the proviso that if v equals zero, R^{17} is hydrogen. Such linear hydride polymers preferably have from about 10 to 100 mole percent Si-H containing siloxy units.

The preferred organohydrogenpolysiloxane resins comprise

(XIX)



and $SiO_{4/2}$ units, where the sum of R and H groups per silicon atom varies from 1.0 to 3.0. Such resins may also include a limited number of difunctional units.

The most preferred organohydrogensiloxanes for use in this invention are hydrogen siloxane resins containing $(H)(CH_3)_2SiO_{1/2}$ units ("M^H" units) and $SiO_{4/2}$ units ("Q" units), wherein the ratio of M^H units to Q units is from about 0.6:1 to about 4:1, preferably 2:1.

These and other suitable organohydrogenpolysiloxanes are well known in the art, for example, as described in U.S. Patent Nos. 3,344,111 and 3,436,366, both of which are incorporated by reference into the present disclosure.

Suitable hydrosilation catalysts are well known in the art, for example, platinum-containing catalysts as described in U.S. Patent Nos. 3,159,601; 3,159,662; 3,220,970; 3,516,946; and 3,814,730, all of which are incorporated by reference into the present disclosure. Other suitable hydrosilation catalysts can be based on the metals rhodium, ruthenium, palladium, osmium, iridium, and platinum. Generally, the olefinically unsaturated

st r can b add d to the organohydrog npolysiloxan in th pr s nce of fr m about 10 to about 500 ppm of catalyst, based on the m tal.

The silicone esters of th present invention are useful in p rsonal car compositions. Exempl s of personal car products which may contain th silicon ster compositions of this inv ntion include lipsticks, ey -shad-
 5 ows, bronzes, blushes, lotions, handcreams, antiperspirants, shampoos, hair conditioners, an emolli nt, an antiseptic, a sunscreen agent, a cleansing agent, hair styling products, hair sprays, spritzes, and other skin care and hair care products.

The silicone esters and silicone ester compositions of the present invention may also be used to soften textile materials. Textile fabrics suitable for treatment with the composition of this invention include, for example,
 10 polyester, polyester cotton, polyester rayon, cotton, rayon, nylon, and the like.

Typically, the novel esters of this invention are used in a silicone-water emulsion which is in turn used as a vehicle for the application of personal care agents or textile-softening agents. The silicone-water emulsion may be either water-in-oil or oil-in-water type emulsions.

Thus, another embodiment of this invention is a water-in-oil type of emulsion wherein the silicone-water
 15 emulsion composition of this invention comprises by weight:

(a) from about 10 to about 70 parts of the liquid silicone ester or mixtures of liquid silicone esters of this invention as a continuous phase;

(b) from about 0.25 to about 10 parts of an emulsifier; and

(c) from about 20 to about 89.75 parts of water as a dispersed phase, wherein the sum of (a), (b), and (c)
 20 is 100 parts.

Another embodiment is an oil-in-water emulsion wherein the silicone-emulsion of this invention comprises by weight:

(a) from about 0.1 to about 60 parts of the liquid silicone ester or mixtures of liquid silicone esters of this invention as a continuous phase;

(b) from about 0.25 to about 10 parts of an emulsifier; and

(c) from about 30 to about 99.65 parts of water as a dispersed phase, wherein the sum of (a), (b), and (c)
 25 is 100 parts.

The silicone-water emulsion compositions of this invention may further comprise polar materials such as those disclosed, for example, in U.S. Patent No. 4,122,029 (Gee et al.), which is hereby incorporated by reference herein. Suitable polar liquids include water, salts, weak acids, weak bases and aqueous solutions there-
 30 of and organic materials bearing polar groups. Emulsion compositions comprising water and/or ethanol are particularly useful.

The silicone-water emulsion composition above may be combined with (d) an effective amount of a personal care agent or a textile softening agent. The term "personal care agent" as used herein refers to an additive
 35 of a cosmetic or medicinal nature which is generally regarded as providing beneficial results when applied externally to the skin of a user. Effective amounts of a personal care agent typically range from about 0.1 to 20,000 parts by weight of the personal care agent per 100 parts of the emulsion. Effective amounts of a textile softening agent typically range from about 0.1 to 5 parts by weight of the textile softening agent per 100 parts of the emul-
 40 sion.

Polar materials of particular interest for the composition of this invention are therefore selected from the group consisting of water, water solutions of polar solutes, polar liquids soluble in water. Suitable water solu-
 45 tions comprise, as the polar solute, inorganic solutes and organic solutes such as sorbitan, alcohols, e.g., glycerine and polyether glycols; nitrogen compounds such as amides, nitriles, and amines; acids; and ethers.

The emulsifying agents used in the personal care or textile softening compositions of this invention may be nonionic, anionic, cationic, or amphoteric but of particular importance are those classes of nonionic emul-
 50 sifiers which are highly ethoxylated. The ethoxylated fatty acids, ethoxylated and non-ethoxylated sorbitan esters, ethoxylated alkyl phenols, and ethoxylated ethers provide the best results.

Examples of suitable emulsifiers for use in the personal care or textile-softening compositions of this invention include those disclosed in U.S. Patent No. 4,784,844 (Thimineur et al.), which is hereby incorporated
 55 by reference herein. The preferred emulsifier for use in the water-in-oil emulsion composition of this invention is a mixture of polysorbate 80 and a silicone polyether copolymer in a cyclic mixture of decamethylcyclopentasiloxane and octamethylcyclotetrasiloxane, the silicone polyether copolymer in cyclic mixture having a viscosity of 3000 centipoise at 25°C and a solids content of 9-11%. The preferred emulsifier for use in the oil-in-water emulsion composition of this inv ntion is DEA-c typhosphat , wh rein DEA repr s nts di thanolamin .

The ord r of mixing of (a)-(d) is not critical, however, particularly satisfactory results can be obtain d when the emulsifying agent and th water ar mix d tog th r in pr bl nd to which th liquid silicon ster is add d. Th p rsonal car ag nt or the textil -treating agent are then added to the resulting composition.

The silicone-water emulsion can be made in th form of a lotion as well as a past or cream-like consist ncy

and can be made further viscous in the form of an ointment, salve, or gel.

The preblend of water-emulsifiable mixture is provided by stirring with moderate heat until a uniform blend is obtained whereupon the liquid silicone ester is added and mixed slowly.

Skin may be treated by the ester compositions of this invention by simply applying the ester composition to the surface of the skin. In treating hair, the ester or composition is applied to the surface of the hair in any suitable manner such as by massaging the composition throughout the hair by hand, by dipping the hair into the composition, or by brushing or combing the ester or composition throughout the hair or by spraying.

In softening textile with the composition of this invention, the composition is applied to at least one surface of the textile fabric in any suitable manner such as by dipping, spraying, or brushing. The applied liquid composition is then heated to a temperature of from above room temperature to less than the melting or decomposition temperature of the textile fabric. Heating can be done by any suitable method or combination of methods, but preferably is done by passing the coated textile through a hot air oven. The coated fabric should be heated for an amount of time sufficient to evaporate any water that is present.

Another embodiment of the present invention is a method for improving the substantivity, water resistance, workability, emollient properties, payout, and solubility in organic compounds of a personal care or textile softening composition, comprising the step of combining the personal care or textile softening composition with an effective amount of the liquid silicone ester of this invention or chemical or physical mixtures of the liquid silicone esters of this invention.

The present invention is also directed to articles comprising a substrate coated with a silicone ester within the scope of this invention or chemical mixtures or physical mixtures of the silicone esters of this invention, or with the personal care or textile softening compositions of this invention. The substrate is preferably skin, hair, plastic, or textile material.

In order to better enable the artisan to practice the present invention, the following examples are provided by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise noted.

Experimental

Example 1

Example 1 illustrates the preparation of a liquid silicone ester within the scope of the present invention.

To a one liter round bottom flask equipped with stirrer, thermometer, and reflux head, there was added 47.43 parts of 95% myristic acid, 19.00 parts of trimethylol propane monoallyl ether (TMPMAE), 0.37 part of p-toluene sulfonic acid as catalyst, and 33.20 parts of a toluene solvent. The mixture was heated to 110-120°C and held there for 4-8 hours, during which time water was removed from the toluene/water azeotrope and the esterification driven to completion. Infrared spectroscopy indicated deletion of the organic acid peak and the presence of the ester. Once the reaction was complete, the p-toluene sulfonic acid catalyst was neutralized with sodium bicarbonate. The resultant ester had a solids content of about 65%.

A platinum-containing catalyst solution (0.029 parts) prepared by reacting octyl alcohol and chloroplatinic acid was then added to the ester prepared above and the resulting mixture was warmed to 120°C at which time about 10.70 parts of a hydrogen-containing siloxane resinous copolymer containing $(\text{CH}_3)_2\text{SiO}_{1/2}$ units ("M" units) and $\text{SiO}_{4/2}$ units ("Q" units) and having a hydrogen content of 0.8 to 1.2% was added. The mixture was heated at reflux until all of the SiH was consumed, as determined by IR analysis. The resultant liquid silicone ester was stripped under vacuum to remove toluene and thereafter filtered while hot through Celite #545 to improve the ester's appearance. The resultant ester product had a solids content of about 100%, a hydrogen content of about 0.01%, and a melting point of +5°C +/- 2°C.

Examples 2-9

Eight liquid silicone esters were prepared as described in Example 1 except that the organic acid, organic alcohol, and organohydrogensiloxane used in the preparation of the esters varied as shown in Table 1 below. The freezing points of the esters prepared in Examples 2-9 are shown in Table 2. These examples illustrate that the esters used in the present invention are liquid at ambient skin temperature.

In Table 1, the term "TMPMAE" represents trimethylol propane monoallyl ether; "M^uQ" represents a hydrogen siloxane resin containing $(\text{H})(\text{CH}_3)_2\text{SiO}_{1/2}$ units and $\text{SiO}_{4/2}$ units, and having a hydrogen content of about 0.8-1.2 weight %; and "SiH Fluid" represents a methylhydrogen siloxane fluid having a hydrogen content of 0.72-1.00 weight % and a viscosity of approximately 35-75 centistokes at 25°C.

TABLE 1**Examples 2-9: Starting Materials**

<u>Example No.</u>	<u>Organic Acid</u>	<u>Organic Alcohol</u>	<u>Organohydrogen-siloxane</u>
2	Stearic Acid	TMPMAE	MHQ
3	Palmitic Acid	TMPMAE	MHQ
4	Myristic Acid	TMPMAE	MHQ
5	Lauric Acid	TMPMAE	MHQ
6	Undecylenic Acid	Stearic	MHQ
7	Undecylenic Acid	Octyl	MHQ
8	Stearic Acid	TMPMAE	SiH Fluid
9	Isostearic Acid	TMPMAE	MHQ

TABLE 2**Examples 2-9: Freezing Points**

<u>Example No.</u>	<u>Freezing Point</u>
2	32°C
3	18°C
4	+5°C
5	-25°C
6	31°C
7	12°C
8	23°C
9	less than -45°C

Example 10 and Comparison Examples A-D

In Example 10 and Comparative Examples A-D, the substantivity and water resistance of the liquid silicone ester prepared in Example 4 (represented as Example 10 in Table 3 below) was compared to the substantivity and water resistance of a polydimethylsiloxane fluid having a viscosity of 350 centistokes at 25°C (Comparison Example A), a siloxane resin containing $(\text{CH}_3)_3\text{SiO}_{1/2}$ units ("M" units) and $\text{SiO}_{4/2}$ units ("Q" units) in polydimethylsiloxane fluid having a viscosity of 50 centistokes (Comparison Example B), isopropyl palmitate (Comparison Example C), and myristyl propionate (Comparison Example D). The substantivity and water resistance properties of these materials were measured by placing side-by-side films of the materials onto a clear polycarbonate substrate and then evaluating the amount of film of each material remaining on the substrate after 5 successive sprays of the films with 250 ml aliquots of water.

The results are shown in Table 3.

TABLE 3
Example 10 and Comparison Examples A-D:
Substantivity and Water Resistance Properties

5

Example No.	% of Film Remaining				
	Aliquot No. 1	Aliquot No. 2	Aliquot No. 3	Aliquot No. 4	Aliquot No. 5
10					
10	100	75-90	50	50	25
Comp. A	0	-	-	-	-
15					
Comp. B	50	25	0	0	-
Comp. C	0	-	-	-	-
Comp. D	25	0	-	-	-

20

In Table 3 above, the "--" indicates that no film remained on the substrate.

The results shown in Table 3 indicate that the liquid silicone esters of the present invention have better substantivity and water resistance properties on plastic surfaces than other silicone and organic esters commonly used in personal care products.

25

Example 11 and Comparative Examples E and F

Example 11 and Comparative Examples E and F illustrate the substantivity to skin of the liquid silicone ester of the present invention. In Example 11, skin is treated with the silicone ester liquid of the present invention; in Comparative Example E, the skin was treated with myristyl propionate; and in Comparative Example F, the skin was left untreated.

Three 5 cm² areas of smooth shaved arm skin were selected and isolated. Each skin section was washed with soap and water and then wiped with isopropyl alcohol to remove soap and residual oil from the skin. The skin section in Example 11 was then treated with 1 gram of the liquid silicone ester prepared in Example 4 which was uniformly spread on the skin section. The skin section in Comparison Example E was treated with 1 gram of myristyl propionate uniformly spread on the surface of the skin. In Comparison Example F, the skin section was left untreated. The skin sections were then immersed in warm water (having a temperature of about 30-35°C) for about 40 minutes with mild movement. The treated skin sections were then allowed to dry.

After drying, each skin section was marked with a yellow felt marker pen and wiped with a soft absorbent tissue. The skin section treated with the liquid silicone ester (Example 11) was wiped clean of the yellow marking, whereas the section treated with myristyl propionate (Comparison Example E) and the untreated skin section (Comparison Example F) both retained the yellow marking. After washing with mild soap and water, the myristyl propionate-treated and untreated skin sections still had visible yellow markings.

The results obtained in Example 11 and Comparison Examples E and F indicate that the liquid silicone ester of the present invention remained on the treated skin in an amount sufficient to prevent the yellow dye from reaching the base skin surface whereas either no amount or an insufficient amount of myristyl propionate remained on the treated skin to prevent the dye from reaching the base skin.

50

Example 12 and Comparison Examples G and H

Three compositions having the formulations shown in Table 4 below were prepared. The term "SF-I" in Table 4 refers to a silicone polyether copolymer in a cyclic mixture of decamethylcyclotetrasiloxane and octamethylcyclotetrasiloxane and having a viscosity of 3000 centipoise at 25°C and a solids content of 9-11%. The term "SF-II" in Table 4 refers to a silicone volatile fluid decamethylcyclotetrasiloxane.

55

TABLE 4
Example 12 and Comparison Examples G and H:
Formulations

5

	<u>Ingredient</u>	<u>Example 12</u>	<u>Comparative Example G</u>	<u>Comparative Example H</u>
10	Part A	<u>Amount (parts by weight)</u>	<u>Amount (parts by weight)</u>	<u>Amount (parts by weight)</u>
	SF-I	10.0	10.0	10.0
15	Liquid Silicone Ester	5.0	0	0
	SF-II	10.0	10.0	10.0
20	Myristyl Propionate	0	0	5.0
25	Part B Polysorbate 80	0.2	0.2	0.2
	Glycerine	3.0	3.0	3.0
	Water	70.8	75.8	70.8
30	NaCl	1.0	1.0	1.0

The compositions shown in Table 4 above were prepared by adding Part B to Part A with high shear agitation and then milling the resulting blend for 1 minute in a homogenizer.

35 Three 5 cm² areas of smooth shaved arm skin were prepared as described in Example 11 and Comparison Examples E and F above. The skin sections were each washed with soap and water and dried, and then wiped with isopropyl alcohol. One skin section was then treated with the composition of Example 12, a second section was treated with the composition of Comparison Example G and a third section was treated with the composition of Comparison Example H. The skin sections were then immersed in warm water (having a temperature of about 30-35°C) for about 40 minutes with mild movement.

40 A yellow felt marking pen was then applied to each of the treated skin sections as described in Example 9 and Comparison Examples E and F. The skin section treated by the composition containing the liquid silicone ester (Example 12) was the only one from which the mark was completely removed by tissue after washing with soap and water.

45 Example 12 and Comparative Examples G and H show that the liquid silicone esters of the present invention have greater substantivity and water resistance than other silicone and organic esters commonly used in personal care products.

Example 13 and Comparative Example I

50 Two compositions having the formulations shown in Table 5 below were prepared.

55

TABLE 5
Example 13 and Comparative Example I: Formulations

<u>Ingredients</u>	<u>Example 13</u>	<u>Comparative Example I</u>
PART A		
Stearic Acid	3.00	3.00
Cetyl Alcohol	2.00	2.00
DEA-Cetylphosphate	2.50	2.50
Octyldimethyl PABA	7.50	7.50
Octyl Salicylate	5.00	5.00
SF-II	5.00	5.00
Liquid Silicone Ester	7.00	-
Isopropyl Myristate	-	7.00
PART B		
Glycerine	4.00	4.00
Dowacil 200	0.10	0.10
Keltrol T	0.35	0.35
Water	63.55	63.55

The compositions of Example 13 and Comparison Example I were prepared by heating Part A and Part B to 85-90°C. Part A was then added to Part B with high shear agitation and the resulting mixture was cooled.

Substantivity and water resistance properties of the compositions prepared in Example 13 and Comparison Example I were measured by placing side-by-side films of the compositions on a panel of polycarbonate substrate and then subjecting the films to six successive sprays of 250 ml aliquots of water. The results are shown in Table 6.

TABLE 6
Example 13 and Comparison Example I:
Substantivity and Water Resistance Properties

<u>Example No.</u>	<u>% of Film Remaining After Spray</u>					
	<u>After 1st spray</u>	<u>After 2nd spray</u>	<u>After 3rd spray</u>	<u>After 4th spray</u>	<u>After 5th spray</u>	<u>After 6th spray</u>
13	100	100	75-90	50	50	25
Comparison Example I	75-90	50	25	*	-	-

* slight haze remained but no observable film

The results shown in Table 6 indicate that the composition containing the liquid silicone ester (Example 13) has better substantivity and water resistance than the composition containing isopropyl myristate.

Exempl 14

Exempl 14 illustrates the preparation of a liquid silicone ester using branched fatty acids.

A liquid silicone ester was prepared by reacting 2 equivalents of isosteric acid with 1 equivalent of trimethylolpropane monoallyl ether (TMPMAE) and then reacting the resulting ester in a hydrosilation reaction with a hydrogen-containing siloxane resinous copolymer containing $(\text{CH}_3)_2\text{HSiO}_{1/2}$ units (M units) and $\text{SiO}_{4/2}$ units (Q units). The resulting branched silicone ester is a liquid.

10 Claims

1. A silicone ester composition comprising a silicone ester or blend of silicone esters, the silicone ester or blend of silicone esters having a melting point of up to about 30°C ., and comprising:

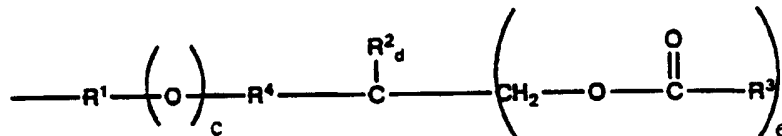
(A) units of the general formula:



wherein R is an organic radical, a is a number ranging from 0 to 3, b is a number ranging from 0 to 3, a+b is a number ranging from 1 to 3, with the proviso that there is present at least one R^E radical, R^E being an ester-containing organic group selected from the group consisting of:

(1)

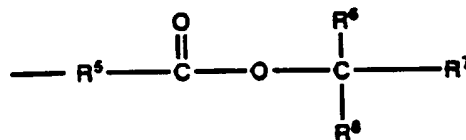
(II)



wherein c is 0 or 1; d is 0, 1, or 2; e is 1, 2, or 3; the sum of d+e being 3; further wherein R^1 is a linear or branched organic group having from 2 to about 14 carbon atoms if the ester-containing organic group (1) contains no olefinic unsaturation and R^1 is a linear or branched organic group having from about 2 to about 18 carbon atoms if the ester-containing organic group (1) contains olefinic unsaturation; further wherein R^2 is hydrogen or an organic radical of from 1 to about 6 carbon atoms; R^3 is a linear unsaturated organic radical of from 1 to about 23 carbon atoms, a linear saturated organic radical of from 1 to about 17 carbon atoms, or a branched organic radical of from about 1 to about 35 carbon atoms; and R^4 is a linear or branched organic radical having 0 to about 6 carbon atoms;

(2)

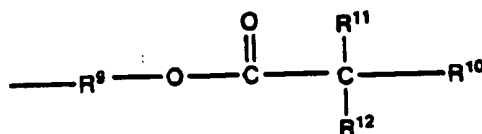
(III)



wherein R^5 is a linear or branched organic group having from 2 to about 15 carbon atoms if the ester-containing organic group (2) contains no olefinic unsaturation and R^5 is a linear or branched organic group having from 2 to about 23 carbon atoms if the ester-containing organic group (2) contains olefinic unsaturation; further wherein R^6 is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms, and R^7 is a linear unsaturated organic radical of from 1 to about 23 carbon atoms, a linear saturated organic radical of from 1 to about 17 carbon atoms, or a branched organic radical of from 1 to about 35 carbon atoms; and R^8 is hydrogen or a linear or branched organic group having from 1 to about 6 carbon atoms;

(3)

(IV)



5

10

15

wherein R⁹ is a linear or branched organic group having from 2 to about 14 carbon atoms if the ester-containing organic group (3) contains no olefinic unsaturation and R⁹ is a linear or branched organic group having from 2 to about 24 carbon atoms if the ester-containing organic group (3) contains olefinic unsaturation; R¹⁰ is a linear unsaturated organic radical of from 1 to about 22 carbon atoms, a linear saturated organic radical of from 1 to about 14 carbon atoms, or a branched organic radical of from 1 to about 34 carbon atoms; R¹¹ is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms; and R¹² is hydrogen or a linear or branched organic radical of from 1 to about 6 carbon atoms; or

(4) chemical reaction mixtures of (1), (2), and (3);

or

(B) R¹³_xR^E_ySiO_{1/2} units and SiO_{4/2} units;

20

wherein each R¹³ is independently an organic radical, x is a number ranging from 0 to 3, y is a number ranging from 0 to 3, x+y is 3, with the proviso that there is present at least one R^E radical; the ratio of R¹³_xR^E_ySiO_{1/2} units to SiO_{4/2} units being from about 0.5:1 to about 4:1.

30

35

40

45

50

55

2. A composition according to claim 1 wherein the liquid silicone ester has a melting point of up to about 25°C.
3. A composition according to Claim 1 or Claim 2 wherein R is an alkyl radical, an aryl radical, an aralkyl radical, or any of the foregoing radicals wherein one or more hydrogen atoms is replaced with a halogen, a cyano radical, or an amino radical.
4. A composition according to any preceding claim wherein R is methyl or a mixture of methyl and phenyl.
5. A composition according to any preceding claim wherein R¹, R⁵ and R⁹ are independently linear or branched alkyl groups having from about 2 to about 12 carbon atoms if the ester-containing organic groups of (A)(1), (A)(2) and (A)(3) respectively, contain no olefinic unsaturation and R¹, R⁵ and R⁹ are independently linear or branched organic groups having from about 2 to about 16 carbon atoms if the ester-containing organic groups of (A)(1), (A)(2) and (A)(3) respectively, contains olefinic unsaturation.
6. A composition according to any preceding claim wherein R² is hydrogen or a linear or branched alkyl group having from 1 to about 5 carbon atoms; R³ is a linear or branched alkyl group having from 8 to about 25 carbon atoms; R⁴ is a linear or branched alkyl group having from 1 to about 5 carbon atoms; R⁶ is hydrogen or a linear or branched alkyl group having from about 1 to about 5 carbon atoms; R⁷ is a linear or branched alkyl group having from about 8 to about 25 carbon atoms; R⁸ is hydrogen or a linear or branched alkyl group having from about 1 to about 5 carbon atoms; R¹⁰ is a linear or branched group, having from about 8 to about 25 carbon atoms; and R¹¹ is hydrogen or a linear or branched alkyl group having from about 1 to about 5 carbon atoms; R¹² is hydrogen or a linear or branched alkyl group having from about 1 to about 5 carbon atoms.
7. A composition according to any preceding claim wherein c is 1, d is 1 and e is 2.
8. A composition according to any preceding claim wherein the ratio of R¹³_xR^E_ySiO_{1/2} units to SiO_{4/2} units being from about 1:1 to about 3:1.
9. A silicone-water emulsion composition selected from :
 - (i) silicone-water emulsions comprising by weight :
 - (a) from about 10 to about 70 parts of the silicone ester composition of any of Claims 1 to 8.
 - (b) from about 0.25 to about 10 parts of an emulsifier; and
 - (c) from about 20 to about 89.75 parts of water as a dispersed phase, wherein the sum of (a), (b) and (c) is 100 parts; or
 - (ii) silicone-water emulsions comprising by weight :
 - (a) from about 0.1 to about 60 parts of the silicone ester composition of Claim 1;

(b) from about 0.25 to about 10 parts of an emulsifier; and
(c) from about 30 to about 99.65 parts of water as a dispersed phase, wherein the sum of (a), (b) and (c) is 100 parts.

- 5 10. A composition according to Claim 12 further comprising (d) an effective amount of a personal care agent or a textile softening agent.
- 10 11. A method for improving the substantivity, water resistance, workability, emollient properties, payout, and solubility in organic compounds of a personal care or textile softening composition, comprising the step of combining the personal care or textile softening composition with an effective amount of the silicone ester composition of any one of Claims 1 to 8.

15

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4636

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 568 566 (TOLENTINO) * claim 1 *	1-8	C08L83/06 D06M15/643 A61K7/06 A61K7/48
X	EP-A-0 299 450 (WACKER) * claim 1 *	1-6,8	
Y	EP-A-0 362 860 (KAO CORP.) * claims 1-5 *	1-11	
Y	EP-A-0 425 121 (DOW CORNING) * claims 1-8 *	1-11	
Y	EP-A-0 363 252 (L'OREAL) * claims 1,10,11 *	1-11	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08L D06M A61K C09D
Place of search THE HAGUE		Date of completion of the search 02 SEPTEMBER 1992	Examiner LENTZ J.C.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 150 (01.92) (P0001)